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STORAGE

THE RETENTION OF SOLUBLE PHOSPHATES IN CALCAREOUS AND NON-CALCAREOUS SOILS

BY

W. H. HARRISON, D.Sc
Imperial Agricultural Chemist

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[Received for publication on 26th April, 1920.]

INTRODUCTION.

THE manner in which the phosphoric acid of superphosphate is absorbed and retained by soils has been the subject of considerable investigation in past years and has given rise to considerable controversy. Storer[1] defines the mode of action of superphosphate as follows :— "When a superphosphate is applied to the soil, the first rainfall, or even the moisture of the soil, dissolves the soluble phosphoric acid, and causes it to soak into the earth. There it comes in contact with carbonate of lime, and with compounds of iron and alumina, and is arrested by these substances. That is to say, the phosphoric acid is precipitated in the earth in the form of phosphate of lime for the most part at first, and of the still more difficultly soluble phosphates of iron and alumina. Unless, indeed, the soil is actually deficient in lime, it is not to be supposed that much of any of the soluble phosphoric acid can remain dissolved in the soil water longer than a few days at the utmost." Again, "It is to be observed that, although the phosphoric acid which has been made soluble with toil and trouble is speedily reprecipitated in the earth, and that although some of the phosphoric acid may eventually be changed then to difficultly soluble forms, the precipitate is nevertheless exceedingly finely divided and very thoroughly disseminated.

[1] "Agriculture in some of its relations with Chemistry," 1897, Vol. I, pp. 364 & 370.

It is far finer than the finest bone-dust; and, what is still more important, it is distributed everywhere in the soil. The roots of the crop are thus provided with a continuous supply of phosphoric acid.....".

The above may be taken as representing the generally accepted view at that time regarding the rôle of superphosphate, and was based upon the observations of several investigators on the rate of reaction between superphosphate solutions and calcium carbonate, and also upon the completeness of the absorption of the soluble phosphoric acid by various soils, particularly those containing a large proportion of carbonate of lime.[1]

Evidence, however, soon accumulated which tended to show that this simple explanation did not entirely agree with observed facts, and it appeared probable that a certain proportion of the absorption could be explained on other than purely chemical grounds. Schroeder,[2] experimenting with intimate mixtures of superphosphate and chalk made into a thick paste, showed that the rate of reversion of the soluble phosphate into insoluble form was exceedingly quick, but that in similar mixtures of soil and superphosphate the fixation was extremely slow and much phosphoric acid remained in solution at the end of 20 days. These two series are, however, not comparable because, in the case of the soils, the amount of superphosphate present was more than sufficient to decompose the whole of the $CaCO_3$ present and still leave an excess in solution, whereas in the former series the reverse conditions held. This experiment cannot be said to have disproved the possibility of retention through the formation of insoluble compounds, but, on the other hand, it points to the existence of another form of absorption when the possibility of the formation of such compounds is removed.

The observation of Pagoul[3] that phosphoric acid was absorbed by soils from solutions of potassium phosphate lent support to an alternative explanation, and this was not only confirmed by the percolation experiments of Schreiner and Failyer[4] but, in addition, they showed that the absorption was subject to laws capable of mathematical expression of a type which indicated the process to be of a physical character. Prescott,[5] later, has shown that the reaction between soil and phosphates obeys the laws of adsorption, but he observes that the phosphate must be kept in solution by using another acid, thus eliminating all possibility of the formation of insoluble calcium phosphates. The

[1] "Agriculture in some of its relations with Chemistry," 1897, Vol. I, p. 364, *et. seq.*
[2] *J. Landw.*, XL, No. 3, p. 213.
[3] *Abst. Expt. Stat. Record*, VI, p. 118.
[4] *U.S.A. Dept. Agri. Bureau of Soils Bull.* 32.
[5] *Jour. Agri. Sci.*, VIII, p. 111.

investigations of Russell and Prescott[1] on the extraction of soils by acid solvents have confirmed the fact that phosphoric acid is adsorbed by soils, but here again the possible influence of calcium carbonate is necessarily removed.

Regarding the possibility of $CaCO_3$ materially affecting the course of the retention of phosphates Pratolongo[2] has shown that there may be two distinct processes at work. With soils containing no lime the absorption of phosphoric acid from mono-calcic phosphate solution is practically instantaneous, but with a soil containing much $CaCO_3$ there is a further slow fixation of P_2O_5 after initial absorption.

From the preceding it will be seen that the retention of phosphoric acid by soils is by no means capable of a satisfactory explanation on purely chemical grounds, and that, in all probability, the phenomenon of adsorption is an important factor. Adsorption is an instantaneous process and, consequently, under conditions which obviate any possibility of the formation of insoluble compounds, may be looked upon as the factor governing the range of distribution of the phosphoric acid through the soil and the availability of the retained phosphate. On the other hand, the introduction of a secondary factor such as the formation of insoluble calcium phosphates must considerably modify the result, but the magnitude of this modification must depend to a large extent upon the rapidity of the reaction concerned. It is conceivable that if, for instance, the rate of the reaction between mono-calcic phosphate and calcium carbonate is very rapid, the range of distribution through a soil will be limited. Conversely, given a very slow rate of reaction the distribution will be wider. Evidence on this point is conflicting, and it is impossible to formulate with any degree of certainty the probable course of events in highly calcareous soils such as are found in Bihar and other portions of the Gangetic system. Consequently, it appeared desirable to institute an investigation to determine, if possible, the predominating factors governing the distribution of soluble phosphates through calcareous and non-calcareous soils, and the results of this investigation form the subject matter of this Memoir.

The enquiry has resolved itself into three distinct divisions, *viz* :—

(1) A study of reaction between mono- and di-calcic phosphates and carbonate of lime.

(2) A determination of the factors governing the retention of soluble phosphates in calcareous and non-calcareous soils.

(3) The distribution of soluble phosphates through calcareous and non-calcareous soils.

[1] *Jour. Agri. Sci.*, VIII, p. 65.
[2] *Le Staz. Sper. Agri.*, 1915, XLVIII, p. 457.

PART I. THE REACTION BETWEEN CALCIUM CARBONATE AND MONO- AND DI-CALCIC PHOSPHATES.

THE importance the reaction between $CaCO_3$ and superphosphate bears in relation to the chemistry of soils was early recognized and has been the subject of considerable study, but, as previously pointed out, the conclusions obtained have been of a very contradictory nature. Meyer[1] digested 10 grams of superphosphate with 300 c.c. water, and added 45 grams of precipitated $CaCO_3$ to the clear filtrate. The mixture was shaken at frequent intervals and tested to determine how much phosphoric acid remained in solution. He found that at the end of six hours 92 per cent. remained in solution, in 24 hours 80 per cent., in 8 days 12 per cent., and in 24 days 2·4 per cent., and concluded that the phosphoric acid of superphosphate is only slowly reverted. Schroeder,[2] however, obtained results which showed a much more rapid reaction, for, at the end of one day only, 4 per cent. remained in solution, and 67 per cent. was present in the citrate-soluble form and 28 per cent. in the insoluble form. Confirmation of this was obtained by Stoklasa,[3] who showed that, by mixing the ingredients in proper proportions, either di- or tri-calcic phosphate could be produced. Davis,[4] on the other hand, concludes from experiments made by him that the soluble P_2O_5 of superphosphate does not attack $CaCO_3$, even when the two are boiled together.

In view of these widely divergent statements it was felt that, as a preliminary, a detailed study of the reaction involved should be made, and this was undertaken in two stages: (*a*) The reaction between mono-calcic phosphate and $CaCO_3$, and (*b*) the reaction between di-calcic phosphate and $CaCO_3$.

A. SUPERPHOSPHATE IN RELATION TO CALCIUM CARBONATE.

One gram of $CaCO_3$ was shaken with 100 c.c. of a solution of monocalcium phosphate for 24 hours, the P_2O_5 present in solution being

[1] Storer. "Agriculture in some of its relations with Chemistry," Vol. I, p. 365.
[2] *Loc. cit.*
[3] *Landw. Ver. Stat.*, XLII, No. 6, p. 439.
[4] *Agri. Jour. India*, 1917, XII, p. 265.

determined before and after. The experimental values are given in Table I.

TABLE I.

Showing the extent to which the P_2O_5 of mono-calcic phosphate is reverted on shaking a solution with $CaCO_3$.

Expt. No.	P_2O_5 in solution before shaking	P_2O_5 in solution after shaking	P_2O_5 removed	Per cent. removed
1	0·4851	0·0113	0·4738	97·7
2	0·4939	0·0115	0·4824	97·7

The removal of P_2O_5 from solution was therefore approximately complete. Further experiments of a similar type were carried out in which the shaking occupied shorter intervals of time.

TABLE II.

Showing the extent to which solutions of mono-calcic phosphate are reverted when shaken with $CaCO_3$ for varying intervals of time.

Expt. No.	Time of shaking	P_2O_5 taken	P_2O_5 left	P_2O_5 removed	Per cent. removed
1	1 hour	0·5680	0·0079	0·5601	98·61
2	2 hours	0·5680	0·0084	0·5596	98·52
3	4 hours	0·5680	0·0060	0·5620	98·94

Consequently it will be seen that the reaction between $CaCO_3$ and superphosphate solutions is a very rapid one and results in practically all the P_2O_5 being rendered insoluble.

The amount of P_2O_5 left in solution is practically constant and of a much higher value than the solubility of tri-calcic phosphate, and leads to the conclusion that, under the conditions of the experiment, the compound formed is of a

more soluble type. Confirmation of this is obtained by *boiling* one gram of $CaCO_3$ with 100 c.c. of superphosphate solution, when it is found that the precipitation is more complete than at ordinary temperatures.

TABLE III.

Showing the effect of boiling solutions of mono-calcic phosphate with $CaCO_3$.

Expt. No.	P_2O_5 before	P_2O_5 after	P_2O_5 removed	Per cent. removed
1	0·4851	0·0002	0·4849	99·96
2	0·4939	0·0011	0·4928	99·78

Under these conditions the reaction becomes practically complete and the amount of P_2O_5 remaining in solution becomes very small. It would, therefore, appear probable that the reaction results in the formation of di-calcic phosphate in the first instance, and then, at the higher temperature, of tri-calcic phosphate :—

$$CaH_4(PO_4)_2 + CaCO_3 = 2CaHPO_4 + CO_2 + H_2O$$
$$2CaHPO_4 + CaCO_3 = Ca_3(PO_4)_2 + CO_2 + H_2O$$

This conclusion is capable of being rigorously tested by determining the amount of CO_2 evolved at ordinary temperatures and at the boiling temperature.

Taking the latter condition first, 0·5 gram of mono-calcic phosphate (94 per cent. purity) was boiled with 0·5 gram of $CaCO_3$ and 75 c.c. water, and the CO_2 evolved absorbed by soda-lime after taking the usual precautions. 0·1514 gram of CO_2 was obtained, whereas theory demanded 0·1650 gram if tri-calcic phosphate were formed, and 0·0825 gram if the di-calcic were formed.

In a second experiment 0·5 gram of calcium biphosphate (pure, Baird & Tatlock, London) containing 56·8 per cent. P_2O_5 was treated as described above and yielded 0·1653 gram CO_2 as against the theoretical 0·1746 gram and 0·0873 gram respectively.

Consequently at boiling temperatures the reaction proceeds to completion with the formation of tri-calcic phosphate.

For the estimation of the CO_2 evolved at ordinary temperatures Hall's[1] apparatus was employed. 15 c.c. of a solution of mono-calcic phosphate,

[1] *J.C.S.*, 1902, LXXI, p. 81.

containing 0·0311 gram of P_2O_5 in solution, were introduced into the reaction bulb of the apparatus into which $CaCO_3$ had been previously introduced. The whole was gently agitated until the manometer reading became constant, and then the tap connecting the secondary bulb was opened and the pressure again read. From the readings obtained the amount of CO_2 evolved was calculated according to the formula given by Hall. The temperature during the experiments was 28°-29°C.

Two duplicate experiments were carried out, and it was found that in one case 5·28 c.c. of CO_2 and in the other 5·91 c.c. were evolved, whilst the theoretical amount required for the formation of di-calcic phosphate from 0·0311 gram P_2O_5 was 4·9 c.c. *Consequently at ordinary temperatures the main product is di-calcic phosphate together with small quantities of tri-calcic phosphate.*

The excess CO_2 over the theoretical was 0·38 c.c. in Experiment I and 1·01 in Experiment II, and, as 44 grams or 22400 c.c. CO_2 represent 142·08 grams P_2O_5 transformed from di- to tri-calcic phosphate, it follows that 0·00241 gram P_2O_5 in Experiment I and 0·00641 gram in Experiment II were fully reverted. *That is, from* 7·7 *to* 20·6 *per cent. of the* P_2O_5 *reverts to tri-calcic phosphate.*

This observation was confirmed by direct analysis, *i.e.*, by the estimation of the di-calcic phosphate produced. It will be shown later that to do this with any pretence to accuracy the extraction with a standard solution of ammonium citrate must be done in the *cold*, otherwise a reaction between $CaCO_3$ and the dissolved phosphate takes place, tri-calcic phosphate being formed and low values for citrate-soluble P_2O_5 obtained.

Experiment I. One hundred c.c. of a solution of mono-calcic phosphate containing 0·5743 gram P_2O_5 were shaken with 1 gram $CaCO_3$ for 24 hours. At the end of that time the insoluble portion was filtered and, after *air-drying*, was extracted in the cold with 100 c.c. of ammonium citrate of sp. gr. 1·09, and the P_2O_5 present as $CaHPO_4$ determined.

P_2O_5 originally present	0·5743 gram
P_2O_5 left in solution	0·0034 „
P_2O_5 reverted	0·5709 „
P_2O_5 extracted by ammonium citrate	0·5521 „
P_2O_5 present as $Ca_3(PO_4)_2$	0·0188 „

∴ 3·27 per cent. of the P_2O_5 was converted into $Ca_3(PO_4)_2$.

Experiment II. Four grams mono-calcic phosphate were shaken with 5 grams $CaCO_3$ and 200 c.c. water for 24 hours and the insoluble residue extracted *twice* with cold ammonium citrate solution.

P_2O_5 originally present		2·2860 grams
P_2O_5 left in solution		0·0086 gram
P_2O_5 reverted		2·2774 grams
P_2O_5 1st extraction	1·3850	
P_2O_5 2nd „	0·4181	
	1·8031	„
P_2O_5 as $Ca_3(PO_4)_2$		0·4743 gram

∴ 20·75 per cent. of the P_2O_5 had reverted to tri-calcic phosphate.

These results are confirmatory of the ones obtained by measuring the amount of CO_2 evolved during the reaction, and it may therefore be taken that, under the experimental conditions, the reaction between $CaCO_3$ and mono-calcic phosphate is a very rapid one and results primarily in the formation of di-calcic phosphate. There then follows a secondary reaction between the di-calcic phosphate and $CaCO_3$ resulting in the formation of a certain proportion of tri-calcic phosphate. Consequently an investigation of the factors which affect the rate of complete reversion to the latter compound must include a study of the reaction between di-calcic phosphate and $CaCO_3$.

B. Di-calcic phosphate in relation to calcium carbonate.

The solubility of di-calcic phosphate, although small, is still very appreciable, as one litre of pure water dissolves 0·136 gram at 25°C., and one litre of saturated CO_2 solution 0·561 gram. It, therefore, follows that the final stage of the retention is a reaction between a comparatively insoluble substance and $CaCO_3$ which will necessarily depend upon the rate at which the former can be brought into solution.

The reaction between $CaCO_3$ and *dissolved* $CaHPO_4$ is very rapid and complete as is shown by the following experiment :—

Two hundred c.c. of a solution of $CaHPO_4$ containing 0·018 gram P_2O_5 were shaken for 24 hours with 1 gram $CaCO_3$, and, at the end of that period, it was found that only 0·0005 gram P_2O_5 remained in solution, *i.e.*, 97 per cent. of the P_2O_5 had been rendered insoluble.

This being the case, the problem resolves itself into a study of the rate at which $CaHPO_4$ changes into $Ca_3(PO_4)_2$ under different conditions. In order

to do this a method of analysis was needed which would differentiate between di- and tri-calcic phosphates, and recourse was had to the well-known ammonium citrate method.

The results obtained in the earlier experiments were very irregular and discordant in character, and this appeared to be due to a reaction taking place between the di-calcic phosphate which had dissolved in the citrate solution and any $CaCO_3$ which might be present. In order to test this, 100 c.c. of a saturated solution of di-calcic phosphate in 1 per cent. ammonium citrate solution were shaken with 1 gram $CaCO_3$ for 24 hours, and the P_2O_5 in solution determined before and after. The original amount present was 0·1244 gram and this was reduced to 0·0908 gram showing a reversion of 27 per cent. Consequently it would appear probable that the standard method of extracting at 65°C. with a solution of ammonium citrate of sp. gr. 1·09 would be liable to error if $CaCO_3$ were present at the same time. This was actually found to be the case.

On the other hand, no indication of any reaction occurring was obtained when a solution of di-calcic phosphate in standard strength ammonium citrate was shaken *in the cold* for 24 hours with $CaCO_3$. The actual values for the P_2O_5 in solution were 0·5310 gram originally and 0·5433 gram at the end. Consequently in all the experiments now considered the determination of di-calcic phosphate present was carried out by extraction with a *cold* solution of ammonium citrate of sp. gr. 1·09.

Reaction between di-calcic phosphate and $CaCO_3$ at 100°*C.* 1·0 gram of di-calcic phosphate, 1·0 gram $CaCO_3$, and 100 c.c. of water were boiled together for periods varying from 15—45 minutes, and the CO_2 liberated determined.

TABLE IV.

Showing the amount of CO_2 evolved when 1 *gram of di-calcic phosphate and* 1 *gram of $CaCO_3$ are boiled together with* 100 *c.c. water.*

Experiment	Time of boiling	CO_2 gram evolved
1	15 minutes	0·1102
2	30 Do.	0·1138
3	45 Do.	0·1104
	Average	0·1115

The di-calcic phosphate employed contained 85·9 per cent. of the pure salt when estimated by the ammonium citrate method, and consequently the theoretical amount of CO_2 to be expected according to the equation $2CaHPO_4 + CaCO_3 = Ca_3(PO_4)_2 + CO_2 + H_2O$ is 0·1098 gram. The values actually obtained are slightly in excess of this but are sufficiently near (+ 0·0017 gram) to show that at high temperatures the reaction proceeds rapidly to a conclusion.

Reaction in the cold. Although the reaction is very rapid and complete at elevated temperatures, it appeared probable that at ordinary temperatures it would be a comparatively slow process. This was confirmed as follows :—

One gram of di-calcic phosphate containing 0·4134 gram of P_2O_5 was shaken with 100 c.c. water and 1 gram $CaCO_3$. Five separate experiments were conducted in which the period of shaking was for 1, 2, 4, 8, and 16 days respectively. At the end of these several periods a determination of the P_2O_5 in solution, the P_2O_5 present as $CaHPO_4$, and the amount present as $Ca_3(PO_4)_2$ was made. The results obtained are given in the following table.

TABLE V.

Showing the extent to which di-calcic phosphate reacts with $CaCO_3$ when shaken together in the presence of water for varying periods of time.

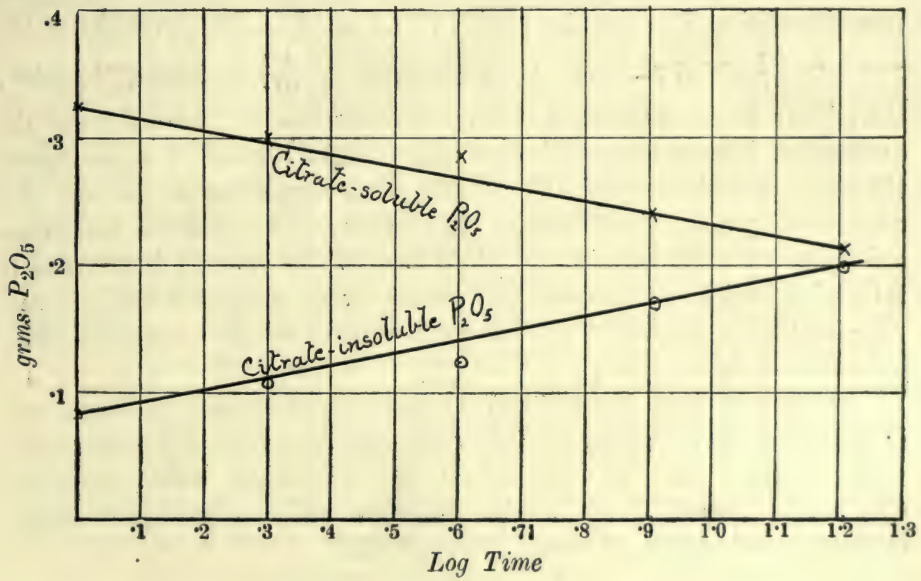
Time of shaking in days (T)	P_2O_5 in solution (W)	P_2O_5 citrate-soluble (D)	P_2O_5 citrate-insoluble (R)	% P_2O_5 reverted to $Ca_3(PO_4)_2$
1	0·0066	0·3246	0·0822	20
2	0·0059	0·2999	0·1076	26
4	0·0034	0·2858	0·1242	30
8	0·0033	0·2399	0·1702	41
16	0·0028	0·2117	0·1989	48
16	0·0341	0·3669	0·0124	Blank experiment. No $CaCO_3$ present.

The presence of a slow progressive reaction is thus demonstrated and, moreover, it is one which proceeds in a well defined manner. It is also noticeable that the amount of P_2O_5 present in solution is much below the normal amount as given by the " blank " experiment and decreases with the period of time.

The relationship between the amount of citrate-soluble P_2O_5 (D) or citrate-insoluble P_2O_5 (R) and the time (T) is a simple semi-logarithmic one as shown by plotting the values of D and R against the log of the time, when the curve produced is a straight line.

DIAGRAM I.

Showing the graph obtained when the amounts of citrate-soluble and citrate-insoluble P_2O_5 are plotted against log time.



Consequently the relationships may be expressed by the general formulæ—

$$\log T = A\,R - K,$$

and $$\log T = k - aD,$$

where A, a, K and k are constants. Employing the values A=10·31, K=0·84, a=10·66, and k=3·464, the calculated and the experimental values are shown in the following table.

TABLE VI.

Containing the calculated and the experimental values for the reversion of di-calcic phosphate.

T	R found	R calculated	Error	D found	D calculated	Error
1	0·0822	0·0815	+ 0·0007	0·3246	0·3253	− 0·0007
2	0·1076	0·1107	− 0·0031	0·2999	0·2970	+ 0·0029
4	0·1242	0·1399	− 0·0157	0·2858	0·2687	+ 0·0171
8	0·1702	0·1690	+ 0·0012	0·2399	0·2404	− 0·0005
16	0·1989	0·1982	+ 0·0007	0·2117	0·2122	− 0·0005

From the relationship log T=AR—K it follows that under the experimental conditions R=0·0815+0·097 log T, and consequently the velocity of the reaction $=\frac{dR}{dT}=0{\cdot}097\,T^{-1}$ and the acceleration is $\frac{d^2R}{dT^2}=-0{\cdot}097\,T^{-2}$ *i. e.*, the velocity of the reaction is in inverse proportion to the time and the acceleration is negative and in inverse proportion to (time).[2] The reaction is, therefore, strongly retarded and can only reach completion at the end of a considerable period of time. This conclusion emerges when there is continuous and intimate contact between the whole mass of the reacting bodies, and it is therefore justifiable to conclude that the conversion of di-calcic into tri-calcic phosphate must proceed at a much slower rate under the conditions which obtain in the soil.

The reaction is in reality one of the formation of tri-calcic phosphate, and in this connection the amount of soluble phosphate present at any moment is of extreme importance. The experimental values obtained clearly show that these values decrease as the reaction progresses, and it is possible to deduce from the relationships previously indicated that

$$W=C-kR,$$

where W=amount of P_2O_5 in solution,

R=amount of P_2O_5 in the citrate-insoluble form,

and C and k are constants.

Taking C=0·0093 and k=0·032 the experimental and the calculated values are contrasted in the following table.

TABLE VII.

Contrasting the experimental and the calculated values for the P_2O_5 in solution (W) when di-calcic phosphate is shaken with $CaCO_3$ and water for varying periods of time.

Time	W calculated	W found	Error
1	0·0067	0·0066	— 0·0001
2	0·0059	0·0059	0·0000
4	0·0053	0·0034	— 0·0019
8	0·0039	0·0033	— 0·0006
16	0·0030	0·0028	— 0·0002

This relationship is of the utmost importance, for it means that the amount of P_2O_5 present in solution decreases in proportion to the formation of tri-calcic phosphate, and this notwithstanding the fact that there is always more than sufficient di-calcic phosphate present to maintain a saturated solution of that substance. The P_2O_5 corresponding to a saturated solution under the experimental conditions is given by the " blank " experiment as 0·0341 gram per 100 c.c. but, in the presence of $CaCO_3$, the values obtained are only 0·0028 to 0·0066 gram, thus showing that the amount in solution is not determined by the di-calcic phosphate present. What determines the actual value is the point to which the reaction has progressed, *i.e.* the amount of $Ca_3(PO_4)_2$ formed, but it is impossible to consider that a very insoluble body of this type can have any direct effect, and this is negatived by the fact that the value of S is not constant. The conclusion is forced that some other product of the reaction is the determining cause. The reaction may be formulated as follows,—

$2CaHPO_4 + CaCO_3 = Ca_3(PO_4)_2 + H_2O + CO_2$, and consequently the only other product which can affect the values of S in proportion to the progress of the reaction is the amount of CO_2 produced, but this substance alone would increase the values rather than lower them The presence of $CaCO_3$, however, materially alters the conditions in that it reacts with the CO_2 forming soluble bicarbonate, thus introducing calcium ions into the solution which would tend to reduce the proportion of P_2O_5 in solution. Under the experimental conditions the CO_2 produced does not escape and, consequently, as the reaction progresses, more and more calcium ions are brought into solution, thus proportionately lowering the amount of dissolved P_2O_5 present.

This brings at once into prominence the relationship between the CO_2 present in the soil gases and the amount of P_2O_5 present in the soil solution. Leather[1] has shown that the soil gases in Pusa soils contain very appreciable amounts of this constituent and, further, that with a very small partial pressure for the CO_2 quite appreciable amounts of $CaCO_3$ go into solution. Consequently calcareous soils,—on the basis of the experimental results now put forward,—will contain a much lower value of P_2O_5, all other things being equal, in the soil solution than in the case of non-calcareous soils. This conclusion was also reached by Leather from the treatment of soils with water, $CaCO_3$ and CO_2, but unfortunately he quotes no experimental data in support.

The above experiments on the rate of reversion of $CaHPO_4$ were carried out by the shaking method in a comparatively large volume of water, and do not approximate to soil conditions where the $CaCO_3$ and di-calcic phosphate are static and where the volume and rate of movement of the water is comparatively small. It seemed very probable that under these conditions the rate of reversion would be considerably reduced, and experiments were carried out to test this.

A mixture of 1 gram di-calcic phosphate containing 0·4134 gram P_2O_5, and 1 gram $CaCO_3$, was made into a paste with 4 c.c. water and stored in test tubes which were sealed so as to be air-tight, and at the end of varying periods of time the contents were examined.

TABLE VIII.

Showing the extent to which reversion occurs in a paste composed of di-calcic phosphate and $CaCO_3$ over varying periods of time.

Time in days	Citrate-soluble P_2O_5 (D)	Citrate-insoluble P_2O_5 (R)	Per cent. reverted
1	0·3934	0·0200	5
2	0·3704	0·0430	10
4	0·3599	0·0535	13
8	0·3316	0·0818	20
16	0·2946	0·1188	29
16	0·4022	0·0112	2·7
		Blank experiment. No $CaCO_3$ present.	

[1] Leather, J. W. "Soil Gases." *Mem. Dept. Agri. India, Chemical Series*, Vol. IV, No. 3. "The System Water, Calcium Carbonate, and Carbonic Acid." *Ibid.*, Vol. I, No. 7.

Under these conditions the amount of reverted P_2O_5 present at the end of 16 days amounts to only 29 per cent. as against 48 per cent. obtained previously, thus demonstrating the fact that *in situ* in soil the rate of reaction is slower.

When the values for citrate-soluble P_2O_5 (D) and citrate-insoluble P_2O_5 (R) are plotted against the logarithm of the time, the resultant graph is a straight line. Consequently the reaction, under these new conditions, is of the same type as that obtained by the shaking method, the only difference being that the velocity is $\frac{2}{3}$ that of the latter. Here, again, the time necessary for the reaction to reach completion is very considerable.

In both of these experiments the CO_2 produced by the reaction does not escape and so has a marked effect on the velocity. In soil the tendency is for the CO_2 to diffuse away and, consequently, if the above conclusions are correct, the rate of reversion would be materially increased.

To test this point, two tubes were taken, each containing 1 gram $CaHPO_4$ (=0·4143 gram P_2O_5), 1 gram $CaCO_3$, and 4 c.c. of water. One tube was sealed up and the other was kept in vacuum over water. In the former 0·1241 gram was reverted, and in the latter 0·1629 gram.

The conclusions derived from a consideration of the foregoing experimental results may be briefly stated as follows :—

1. The reaction between calcium carbonate and mono-calcic phosphate at ordinary temperatures is a very rapid one resulting in the formation of di-calcic phosphate together with small quantities of tri-calcic phosphate.

2. Di-calcic phosphate *when present in solution* also rapidly reacts with calcium carbonate to form tri-calcic phosphate. The reaction between solid di-calcic phosphate and $CaCO_3$ in the presence of water is, however, much slower in character, and a considerable period of time is necessary for its completion.

3. During the course of the reaction CO_2 is produced which, by increasing the number of calcium ions in solution, reduces very materially the quantity of P_2O_5 formed in solution. Consequently, with calcareous soils the importance of cultural conditions which will tend to keep the CO_2 content of the soil gases at a minimum and thus permit of a greater concentration of P_2O_5 in the soil solution is apparent.

4. Assuming that the P_2O_5 of superphosphate may be retained in soils both by adsorption and by chemical combination, the rapidity of the reaction with $CaCO_3$ would lead to the conclusion that the retention in calcareous soils will be determined mainly by the latter factor.

PART II. THE FACTORS GOVERNING THE RETENTION OF SOLUBLE PHOSPHATES IN CALCAREOUS AND NON-CALCAREOUS SOILS.

In Part I it has been demonstrated that the rate of reaction between solutions of mono-calcic phosphate and $CaCO_3$ is a very rapid one resulting in the formation of the comparatively insoluble di-calcic phosphate. The latter in turn slowly reacts with further quantities of $CaCO_3$ forming tri-calcic phosphate. Consequently it would appear probable that this reaction must play a prominent part in calcareous soils in retaining those forms of soluble phosphates which are capable of reacting, but, on the other hand, the effect of this chemical retention would be at a minimum in non-calcareous soils, and in these circumstances adsorption may be the determining factor.

It is of the utmost importance to determine which of these modes of retention is the predominant factor in the two types of soil, for not only must the "availability" of the retained phosphoric acid be very dissimilar in the two cases, but the distribution through the mass of the soil must also be very different.

With this object in view parallel series of experiments were carried out with a Pusa soil representing highly calcareous soils, and a soil from Kalianpur which is almost devoid of lime.

The chemical and physical composition of these soils is contrasted in the following table.

Table IX.

Giving chemical and physical composition of Pusa and Kalianpur soils.

Constituents	Kalianpur soil	Pusa soil
A. Chemical composition		
Sand and insoluble matter	86·36	56·40
Al_2O_3	4·04	2·80
Fe_2O_3	3·23	2·70
Mn_3O_4	0·04	0·07
CaO	0·81	18·30
MgO	1·14	1·65
K_2O	0·69	0·51
Na_2O	0·29	0·19
P_2O_5	0·38	0·11
SO_3	0·03	0·02
CO_2	0·13	14·33
Moisture	1·26	0·87
Organic matter	1·60	2·05
Total	100·00	100·00

TABLE IX.—*concld.*

Constituents	Kalianpur soil	Pusa soil
A. CHEMICAL COMPOSITION—*Concld.*		
N	0·018	0·067
Humus	1·15	1·00
Available K_2O	0·0344	0·0109
Available P_2O_5	0·3237	0·0003
$CO_2 = CaCO_3$	0·284	32·57
B. MECHANICAL ANALYSIS		
Fine gravel	40·06	19·64
Sand	32·70	45·83
Fine sand	7·61	16·50
Silt	6·87	9·43
Fine silt	10·74	7·60
Clay	2·02	1·00
Total	100·00	100·00

Following the usual method of experiment for the recognition of adsorption, 100 grams of soil were shaken for one hour with one litre of water containing varying concentrations, within very wide limits, of soluble P_2O_5 derived from mono-calcium phosphate. At the end of this period the soil was separated from the solution by suction filtration and the concentration of the P_2O_5 remaining in solution determined.

Unfortunately no means were available for the maintenance of a rigorously controlled temperature, but this difficulty was surmounted to a considerable extent by carrying out all the experiments with the one soil at the same time, and under the same conditions, in a room which was not subjected to sudden changes of temperature. Notwithstanding small irregularities induced by slight differences in the conditions between one vessel and another the results obtained were very concordant.

Where adsorption phenomenon occurs, the distribution of a dissolved substance between the solvent and the adsorbing medium is regulated according to the expression,—

$$\frac{x}{m} = K S^{\frac{1}{n}},$$

where $\frac{x}{m}$ = amount of substance removed from solution (retained) per unit mass of adsorbent (soil),

S=concentration of the substance in the solvent *after* adsorption has taken place,

and K and p are constants.

For the sake of uniformity in contrasting the experimental results this expression may be written—

$$R = K\, S^{\frac{1}{p}},$$

where R=m.gr. of substance retained per 1000 grams soil,

and S=m.gr. of substance per 1000 c.c. solvent.

Then $\log R = k + \frac{1}{p} \log S$, where $k = \log K$.

Consequently if the distribution of the dissolved substance between the solution and the soil obeys the adsorption laws, the curve obtained by plotting the values of log R against log S is a straight line. This is the test mainly relied upon by us in interpreting the results obtained.

The data obtained in the series of experiments where 100 grams of soil were shaken with 1000 c.c. of solution are as follows :—

TABLE X.

Showing distribution of P_2O_5 as superphosphate between soil and solution using 100 *grams soil and* 1000 *c.c. solution.*

(m.gr. P_2O_5.)

A. KALIANPUR SOIL

P_2O_5 originally in solution	P_2O_5 in solution after shaking	P_2O_5 retained by soil	S	R
4	2·8	1·2	2·8	·12
16	10·5	5·5	10·5	55
64	41·5	22·5	41·5	225
256	174·7	81·3	174·7	813
1024	749·7	274·3	749·7	2743

TABLE X.—*concld.*

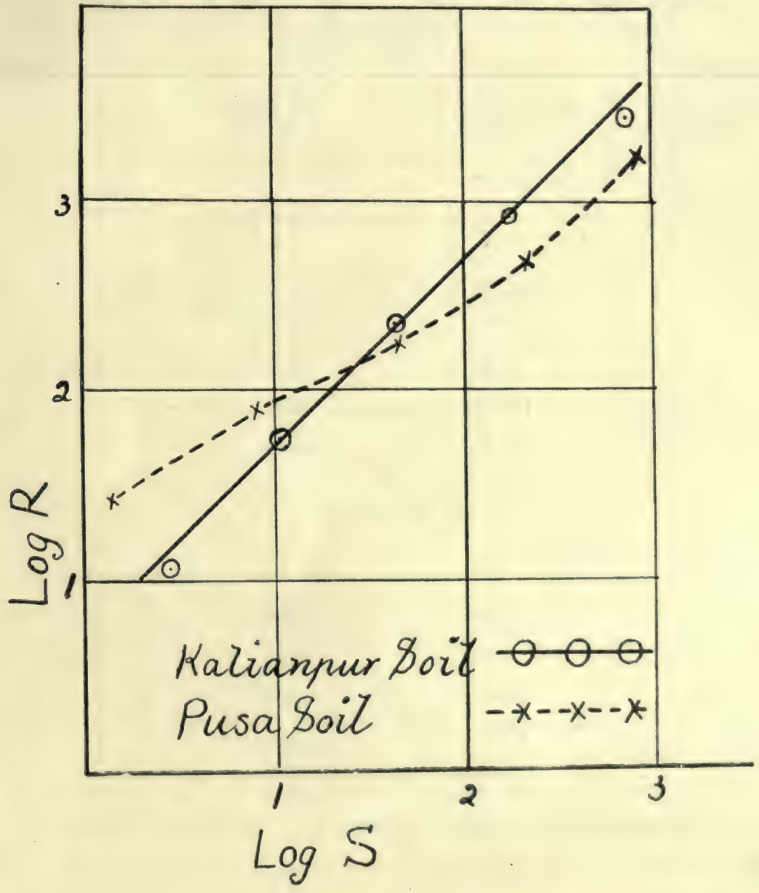
B. PUSA SOIL

P_2O_5 originally in solution	P_2O_5 in solution after shaking	P_2O_5 retained by soil	S	R
4	1·4	2·6	1·4	26
16	8·1	7·9	8·1	79
64	46·8	17·2	46·8	172
256	209·0	47·0	209·0	470
1024	859·1	164·9	859·1	1649

The logarithmic curves obtained by plotting log R against log S are shown in Diagram II.

DIAGRAM II.

Showing curves obtained by plotting log R against log S.



It will be seen that the values for the Kalianpur soil fall upon a straight line, whereas those for the Pusa soil are on a well defined sinuous curve. It is, therefore, permissible to conclude that, under the experimental conditions, the P_2O_5 of superphosphate is mainly retained through adsorption in non-calcareous soils, whereas the retention is mainly due to other causes in the case of calcareous soils.

In order to obtain confirmation of these conclusions a second series of experiments were carried out in which 250 grams of soil were shaken with 1 litre of solution. The experimental conditions were similar to the preceding and the results are given in Table XI.

TABLE XI.

Showing distribution of P_2O_5 from superphosphate between soil and solution using 250 grams soil and 1000 c.c. solution.

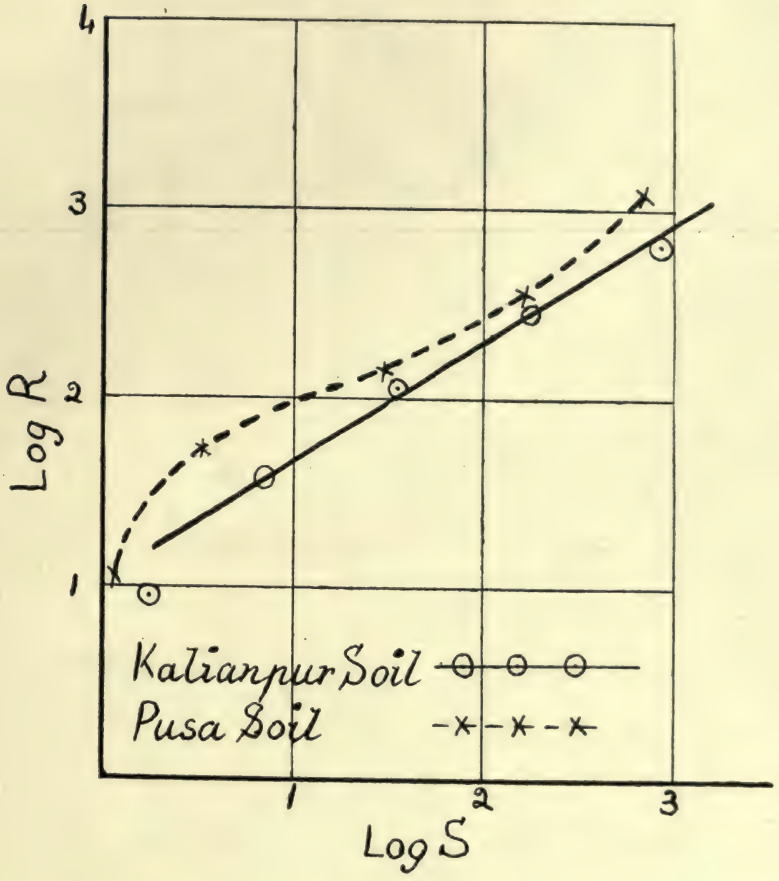
(m.gr. P_2O_5.)

P_2O_5 originally in solution	P_2O_5 remaining in solution	P_2O_5 retained by soil	S	R
	A. KALIANPUR SOIL			
4	1·8	2·2	1·8	8·8
16	6·6	9·4	6·6	37·6
64	35·5	28·5	35·5	114·0
256	187·0	69·0	187·0	276·0
1024	864·4	159·6	864·4	638·4
	B. PUSA SOIL			
4	1·2	2·8	1·2	11·2
16	3·2	12·8	3·2	51·2
64	29·6	34·4	29·6	137·6
256	167·6	88·4	167·6	353·6
1024	718·0	306·0	718·0	1224·0

The logarithmic curves obtained from the values of S and R are shown in Diagram III.

DIAGRAM III.

Showing curves obtained by plotting log R against log S.



These results confirm the ones previously considered and support the conclusion that in non-calcareous soils the retention of the P_2O_5 is mainly due to adsorption, whereas in calcareous soils retention by adsorption is either non-existent or entirely masked by other causes.

Support to the conclusion that retention of superphosphate by calcareous soils is due to chemical combination is derived from experiments made by agitating the type soils with solutions of di- and tri-sodium phosphates, where in all cases the retention obeys the adsorption laws. In this case no chemical reaction could be demonstrated between $CaCO_3$ and the sodium phosphates.

Taking the adsorption from di-sodium phosphate first, 250 grams of soil were agitated for one hour with one litre of solutions of varying concentration and the P_2O_5 remaining in solution was then determined. The following results were obtained :—

TABLE XII.

Showing distribution of P_2O_5 between soil and solvent when di-sodium phosphate is used.

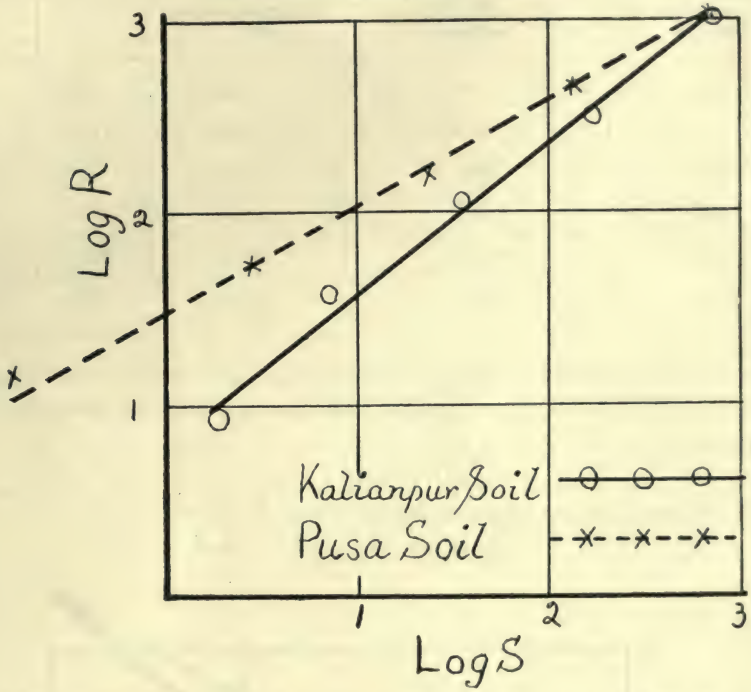
(m.gr. P_2O_5).

P_2O_5 originally present	P_2O_5 remaining in solution	P_2O_5 retained by soil	S	R
	A. KALIANPUR SOIL			
4	1·9	2·1	1·9	8·4
16	6·6	9·4	6·6	37·6
64	35·6	28·4	35·6	113·6
256	178·2	77·8	178·2	311·2
1024	770·9	253·1	770·9	1012·4
	B. PUSA SOIL			
4	0·16	3·84	0·16	15·36
16	2·7	13·3	2·7	53·2
64	24·3	39·7	24·3	158·8
256	140·2	115·8	140·2	463·2
1024	732·1	291·9	732·1	1167·6

The curves obtained by plotting log R against log S are shown in Diagram IV.

DIAGRAM IV.

Showing curves produced by plotting log R against log S when di-sodium phosphate is used.



It follows therefore that di-sodium phosphate is retained in both calcareous and non-calcareous soils by adsorption.

A similar experiment with tri-sodium phosphate and 200 grams soil gave the following results.

TABLE XIII.

Showing distribution of P_2O_5 between soil and solvent when tri-sodium phosphate is used.

(m.gr. P_2O_5.)

A. KALIANPUR SOIL

P_2O_5 originally in solution	P_2O_5 remaining in solution	P_2O_5 retained by soil	S	R
16	7·8	8·2	7·8	41·0
64	35·3	28·7	35·3	143·5
128	90·9	37·1	90·9	185·5
256	170·2	85·8	170·2	429·0
512	352·8	159·2	352·8	796·0
1024	735·6	288·4	735·6	1442·0

TABLE XIII.—*concld.*

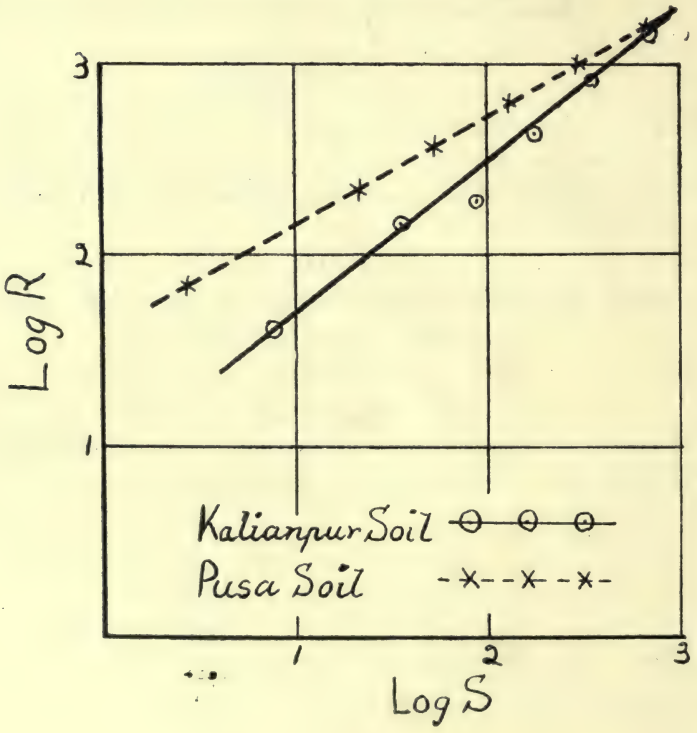
B. PUSA SOIL

P^2O_5 originally in solution	P_2O_5 remaining in solution	P_2O_5 retained by soil	S	R
16	2·8	13·2	2·8	66·0
64	21·5	42·5	21·5	212·5
128	52·9	75·1	52·9	375·5
256	130·5	125·5	130·5	627·5
512	305·2	206·8	305·2	1034·0
1024	709·1	314·9	709·1	1574·5

The curves obtained by plotting log R against log S are shown in Diagram V. In both cases the points lie on straight lines showing that the retention is due to adsorption.

DIAGRAM V.

Showing curves produced on plotting log R against log S when tri-sodium phosphate is used.



It may, therefore, be concluded that soluble phosphates which do not readily react with calcium carbonate are retained through adsorption in both calcareous and non-calcareous soils.

Summary.

1. Soluble phosphates which do not react with $CaCO_3$ are retained by adsorption in both calcareous and non-calcareous soils.

2. Soluble phosphates of the type of mono-calcic phosphate which readily react with $CaCO_3$ are retained through adsorption in non-calcareous soils. In calcareous soils, on the other hand, the experimental values obtained show that other factors than adsorption come into play.

PART III. THE DISTRIBUTION OF SOLUBLE PHOSPHATES THROUGH CALCAREOUS AND NON-CALCAREOUS SOILS.

It has been shown in the preceding section that in non-calcareous soils the retention of the P_2O_5 of superphosphate is due to adsorption, whereas in calcareous soils other factors come into play which are probably due to chemical combination. The experimental evidence hitherto adduced is insufficient to determine if chemical factors are the ones which mainly determine the retention in the latter type of soil, or whether the phenomenon of adsorption has still an important bearing on the question.

When the rapidity of the reaction between superphosphate and calcium carbonate is taken into account, it is impossible to throw aside the hypothesis that this reaction must be the determining factor under circumstances in which it can occur and, if this is correct, then it would appear that when superphosphate is applied to a calcareous soil, comparatively insoluble calcium phosphates are immediately formed *in situ*, thus limiting the distribution of the P_2O_5 through the soil and causing the superphosphate to have a very localized value. On the other hand, in non-calcareous soils, as the retained P_2O_5 is a function of the P_2O_5 remaining in solution, it would appear probable that the range of action would be wider and the distribution more uniform throughout the mass of the soil.

In order to test the validity of these conclusions the following experiments were carried out. A solution of superphosphate (about 1 per cent. strength) was allowed to percolate through columns of the type soils of 20 inches depth contained in glass tubes, the bottom of which was closed by a fine wire gauze. After all the solution had passed into the column of soil the whole was allowed to stand for a further period of about 3 days until percolation ceased. The tube was then cut into 2″ sections and the soil in each section removed and rapidly washed on the filter pump with a small quantity of water so as to remove the solution. The amount of P_2O_5 contained in the solution was then determined. The washed soil was rapidly dried, gently ignited to remove organic matter and the total P_2O_5 contained estimated. The difference between this value and the original one for the soil gives the amount of P_2O_5 retained by the soil in that section. The object in view in adopting this procedure was to obtain, if possible, an approximate idea of the proportion of P_2O_5 retained by each section of soil to the P_2O_5 in the soil solution. In the case of the Kalianpur soil, where adsorption is the determining factor, the relation at best could only be

very approximate, but it was hoped that more accurate data would be forthcoming in the case of the Pusa soil. Unfortunately, for the completion of each series there was involved a total of twenty-one separate determinations, and it was found that the sum of the P_2O_5 in the soil solution, the P_2O_5 present in the percolate, and the P_2O_5 retained by the soil did not equal the amount of P_2O_5 originally taken. This error varied from $7\frac{1}{2}$ to 17 per cent. and, although a large part of it was due to the accumulated errors of many separate determinations, yet a portion was probably due to the formation of very insoluble compounds as shown by experiments in which the tubes were cut and only the total P_2O_5 held in each section determined. In the latter series the error was reduced from $3\frac{1}{2}$ to $9\frac{1}{2}$ per cent.

As the amount of P_2O_5 present in the percolate could be determined with considerable accuracy, the amounts in deficit must have been held in the columns of soil and, accordingly for purposes of comparison, it has been distributed amongst the soil sections in proportion to the P_2O_5 held in each section. Although the errors involved are large, the great difference in the character of the results obtained from the two types of soil is so distinct that it does not affect the validity of the conclusions drawn. The results obtained are given in Tables XIV and XV.

TABLE XIV.

Showing the results obtained from the percolation of superphosphate solution through Pusa and Kalianpur soils.

Section	P_2O_5 present in solution	P_2O_5 present in insoluble form	P_2O_5 present originally in soil	P_2O_5 retained by soil	Total P_2O_5 held in section	Remarks		Corrected value for total P_2O_5 held in section	Per cent. of original P_2O_5 held in section
				PUSA SOIL (dry)			grm. P_2O_5		
0″– 2″	0·0291	0·7409	0·0404	0·7005	0·7296	Percolate ..	0·0024	0·8915	66·5
2″– 4″	0·0192	0·1208	,,	0·0804	0·0996	Soil solution ..	0·1319	0·1217	9·1
4″– 6″	0·0176	0·0882	,,	0·0478	0·0654	Retained ..	0·9632	0·0799	6·0
6″– 8″	0·0150	0·0759	,,	0·0355	0·0505			0·0617	4·6
8″–10″	0·0139	0·0741	,,	0·0337	0·0476	Total ..	1·0975	0·0583	4·3
10″–12″	0·0115	0·0723	,,	0·0319	0·0434	P_2O_5 taken ..	1·3408	0·0530	4·0
12″–14″	0·0089	0·0503	,,	0·0099	0·0188	Error for distribution ..	0·2433	0·0230	1·7
14″–16″	0·0071	0·0529	,,	0·0125	0·0196			0·0240	1·8
16″–18″	0·0055	0·0428	,,	0·0024	0·0079			0·0097	0·7
18″–20″	0·0041	0·0490	,,	0·0086	0·0127			0·0156	1·2
Total	0·1319	1·3672	0·4040	0·9632	1·0951	....		1·3384	

TABLE XIV.—*contd.*

Section	P_2O_5 present in solution	P_2O_5 present in insoluble form	P_2O_5 present originally in soil	P_2O_5 retained by soil	Total P_2O_5 held in section	REMARKS	grm. P_2O_5	Corrected value for total P_2O_5 held in section	Per cent. of original P_2O_5 held in section
				PUSA SOIL (moist)					
0″– 2″	0·0143	0·3418	0·0178	0·3240	0·3383			0·3764	73·7
2″– 4″	0·0084	0·0496	,,	0·0318	0·0402	Percolate ..	0·0000	0·0447	8·8
4″– 6″	0·0053	0·0342	,,	0·0164	0·0217	Soil solution ..	0·0399	0·0241	4·7
6″– 8″	0·0046	0·0340	,,	0·0162	0·0208	Retained ..	0·4190	0·0231	4·5
8″–10″	0·0040	0·0313	,,	0·0135	0·0175	Total ..	0·4589	0·0196	3·8
10″–12″	0·0030	0·0296	,,	0·0118	0·0148	P_2O_5 taken ..	0·5106	0·0165	3·2
12″–14″	0·0003	0·0199	,,	0·0021	0·0024	Error for distribution ..	0·0517	0·0027	0·5
14″–16″	nil	0·0190	,,	0·0012	0·0012			0·0013	0·25
16″–18″	nil	0·0188	,,	0·0010	0·0010			0·0011	0·2
18″–20″	nil	0·0188	,,	0·0010	0·0010			0·0011	0·2
Total	0·0399	0·5970	0·1780	0·4190	0·4589			0·5106	
				KALIANPUR SOIL (dry)					
0″– 2″	0·0375	0·1447	0·0754	0·0693	0·1068			0·1312	16·5
2″– 4″	0·0254	0·1332	,,	0·0578	0·0832	Percolate ..	0·0348	0·1022	12·9
4″– 6″	0·0249	0·1389	,,	0·0635	0·0884	Soil solution ..	0·2215	0·1086	13·7
6″– 8″	0·0221	0·1217	,,	0·0463	0·0684	Retained ..	0·3963	0·0840	10·6
8″–10″	0·0199	0·1169	,,	0·0415	0·0614	Total ..	0·6526	0·0754	9·5
10″–12″	0·0218	0·1063	,,	0·0309	0·0527	P_2O_5 taken ..	0·7938	0·0647	8·2
12″–14″	0·0205	0·1094	,,	0·0340	0·0545	Error for distribution .	0·1412	0·0670	8·4
14″–16″	0·0181	0·0975	,,	0·0221	0·0402			0·0494	6·2
16″–18″	0·0163	0·0913	,,	0·0159	0·0322			0·0396	5·0
18″–20″	0·0150	0·0904	,,	0·0150	0·0300			0·0369	4·6
Total	0·2215	1·1503	0·7540	0·3963	0·6178			0·7590	

TABLE XIV.—*concld.*

Section	P_2O_5 present in solution	P_2O_5 present in insoluble form	P_2O_5 present originally in soil	P_2O_5 retained by soil	Total P_2O_5 held in section	Remarks		Corrected value for total P_2O_5 held in section	Per cent. of original P_2O_5 held in section
				KALIANPUR SOIL (moist)			grm. P_2O_5		
0″– 2″	0·0359	0·1632	0·0731	0·0901	0·1260			0·1541	19·3
2″– 4″	0·0318	0·1508	,,	0·0777	0·1095	Percolate ..	0·0008	0·1339	16·7
4″– 6″	0·0271	0·1261	,,	0·0530	0·0801	Soil solution ..	0·2220	0·0980	12·3
6″– 8″	0·0254	0·1208	,,	0·0477	0·0731	Retained ..	0·4306	0·0894	11·2
8″–10″	0·0221	0·1054	,,	0·0323	0·0544			0·0666	8·3
10″–12″	0·0207	0·1050	,,	0·0319	0·0526	Total ..	0·6534	0·0644	8·0
12″–14″	0·0201	0·1019	,,	0·0288	0·0489	P^2O_5 taken ..	0·7991	0·0598	7·5
14″–16″	0·0168	0·1006	,,	0·0275	0·0443	Error for distri-		0·0542	6·8
16″–18″	0·0124	0·0983	,,	0·0252	0·0376	bution ..	0·1457	0·0460	5·7
18″–20″	0·0097	0·0895	,,	0·0164	0·0261			0·0319	4·0
Total	0·2220	1·1616	0·7310	0·4306	0·6526			0·7983	

TABLE XV.

Showing results obtained when only the total P_2O_5 held in each section is determined.

Section	P_2O_5 present in each section	P_2O_5 originally present in soil	P_2O_5 held in each section	Remarks		Corrected value for P_2O_5 held in each section	Per cent. of P_2O_5 taken held in each section
		PUSA SOIL			grm. P_2O_5		
0″– 2″	0·5495	0·0194	0·5301	Percolate ..	0·0049	0·5518	69·8
2″– 4″	0·0732	,,	0·0538	P_2O_5 retained		0·0560	7·1
4″– 6″	0·0591	,,	0·0397	in sections .	0·7578	0·0413	5·2
6″– 8″	0·0547	,,	0·0353			0·0368	4·6
8″–10″	0·0468	,,	0·0274	Total ..	0·7627	0 0286	3·6
10″–12″	0·0397	,,	0·0203	P_2O_5 taken .	0·7938	0·0212	2·7
12″–14″	0·0344	,,	0·0150			0·0156	2·0
14″–16″	0·0318	,,	0·0124	Error ..	0·0311	0·0129	1·6
16″–18″	0·0300	,,	0·0106			0·0110	1·4
18″–20″	0·0326	,,	0·0132			0·0137	1·7
Total	0·9518	0·1940	0·7578			0·7889	

TABLE XV.—*concld.*

Section	P_2O_5 present in each section	P_2O_5 originally present in soil	P_2O_5 held in each section	REMARKS		Corrected value for P_2O_5 held in each section	Per cent. of P_2O_5 taken held in each section
		KALIANPUR SOIL			grm. P_2O_5		
0″– 2″	0·1535	0·0343	0·1192	Percolate ..	0·0271	0·1318	16·6
2″– 4″	0·1561	,,	0·1218	P_2O_5 retained		0·1344	17·0
4″– 6″	0·1270	,,	0·0927	in sections..	0·6942	0·1024	12·9
6″– 8″	0·1164	,,	0·0821		———	0·0907	11·4
8″–10″	0·1058	,,	0·0715	Total ..	0·7213	0·0790	10·0
10″–12″	0·0820	,,	0·0477	P_2O_5 taken .	0·7938	0·0527	6·6
12″–14″	0·0820	,,	0·0477		———	0·0527	6·6
14″–16″	0·0759	,,	0·0416	Error ..	0·0725	0·0459	5·8
16″–18″	0·0706	,,	0·0363			0·0400	5·0
18″–20″	0·0679	,,	0·0336			0·0371	4·7
Total	1·0372	0·3430	0·6942			0·7667	

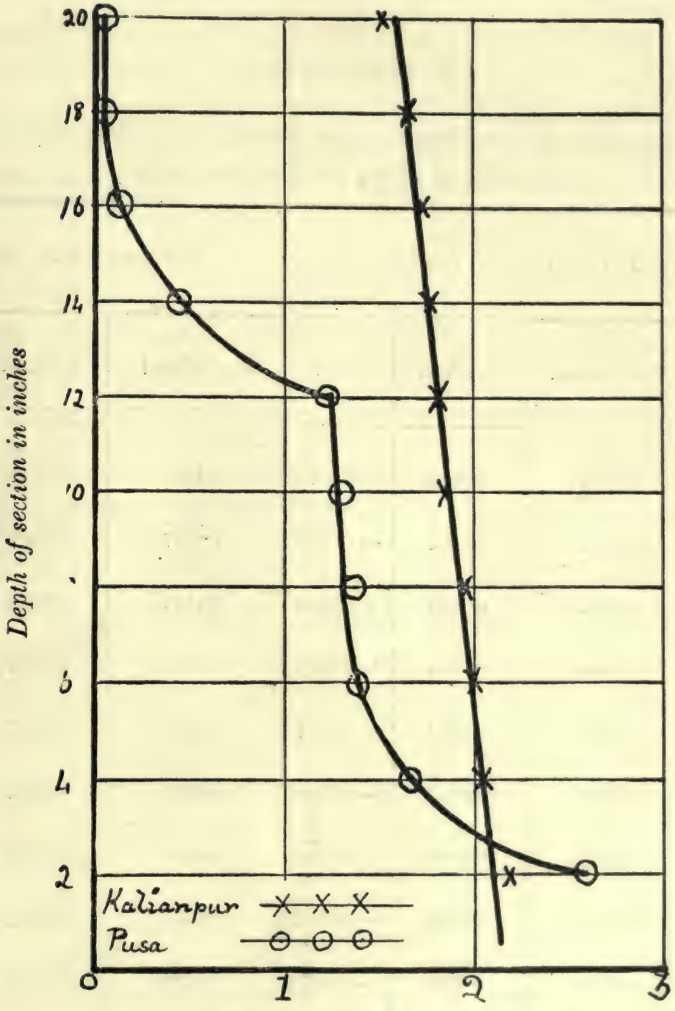
That the cause of the retention of superphosphate and the consequent range of action of the latter is very dissimilar in the two soils is clearly demonstrated by these results. In the first place the amount of P_2O_5 which is retained in each successive layer of the Pusa soil decreases very rapidly until the 12″—14″ layer is reached when the retention is practically completed, and the percolates contain either none or only very small amounts of P_2O_5. Furthermore, of the total P_2O_5 held by each section 67 to 74 per cent. is held in the first two inches, and 76 to 83 per cent. in the first four inches.

On the other hand, the Kalianpur soil shows no break in continuity throughout the whole depth of the soil; the percolate contains as much as 27 per cent. of the P_2O_5 originally taken, the first layer of the soil only retains 17 to 19 per cent. of P_2O_5, and the first four inches only retains 29 to 36 per cent.

These differences are made more pronounced when a detailed study of the values obtained is made. Taking the case of the Kalianpur soil first it is found that if the logarithm of the total value for the P_2O_5 held in any section, *i.e.*, the sum of the soluble and the retained P_2O_5, is plotted against the depth, the points lie about a straight line, whereas in the case of the Pusa soil the points lie on a curve broken at the 12″—14″ section. The curves obtained for the "moist" soils are given in Diagram VI.

DIAGRAM VI.

Showing curves produced on plotting log total m.gr. P_2O_5 held in each section against the depth.



Consequently the relationship—

log T=a—kd holds good for the Kalianpur soil,

where T=m.gr. total P_2O_5 held in a section,

d=depth of the section in inches,

and a and k are constants.

It will be found that the values a=2·18 and k=0·0303 fit the results very closely in the case of the dry soil, and a=2·28 and k=0·0385 hold for the moist soil. The following table contrasts the calculated and the experimental values.

TABLE XVI.

Showing the calculated and the experimental values obtained for the total quantity of P_2O_5 held in each section.

	KALIANPUR SOIL (dry)			KALIANPUR SOIL (moist)		
d	T calculated	T found	Error	T calculated	T found	Error
2	0·1316	0·1312	— 0·0004	0·1596	0·1541	— 0·0055
4	0·1145	0·1022	— 0·0123	0·1337	0·1339	+ 0·0002
6	0·0996	0·1086	+ 0·0090	0·1119	0·0980	— 0·0139
8	0·0866	0·0840	— 0·0026	0·0938	0·0894	— 0·0044
10	0·0753	0·0754	+ 0·0001	0·0785	0·0666	— 0·0119
12	0·0655	0·0647	— 0·0008	0·0658	0·0644	— 0·0014
14	0·0570	0·0670	+ 0·0100	0·0551	0·0598	+ 0·0047
16	0·0496	0·0494	— 0·0002	0·0461	0·0542	+ 0·0081
18	0·0431	0·0396	— 0·0035	0·0386	0·0460	+ 0·0074
20	0·0375	0·0369	— 0·0006	0·0324	0·0319	— 0·0005

The formula log T=a−kd can, of course, be put into the exponential form : $T=Ae^{-kd}$, and consequently the relationship between the concentration

of P_2O_5 and depth follows the ordinary "compound interest" law. In other words, in non-calcareous soils the amount of the P_2O_5 of superphosphate retained in any soil layer, when percolating downwards in the soil solution, diminishes in geometrical proportion as the depth increases in arithmetical proportion, a conclusion which is in accordance with retention by physical agencies.

From the formula log T=a—kd the total quantity of P_2O_5 in milligrams (H) held in a column of soil down to a depth d can be shown to be equal to K (l—a^d), where K and a are constants respectively equal to 0·940 and 0·925 in the case of the dry soil, and 0·915 and 0·912 for the moist soil. The following table compares the calculated and the experimental values.

TABLE XVII.

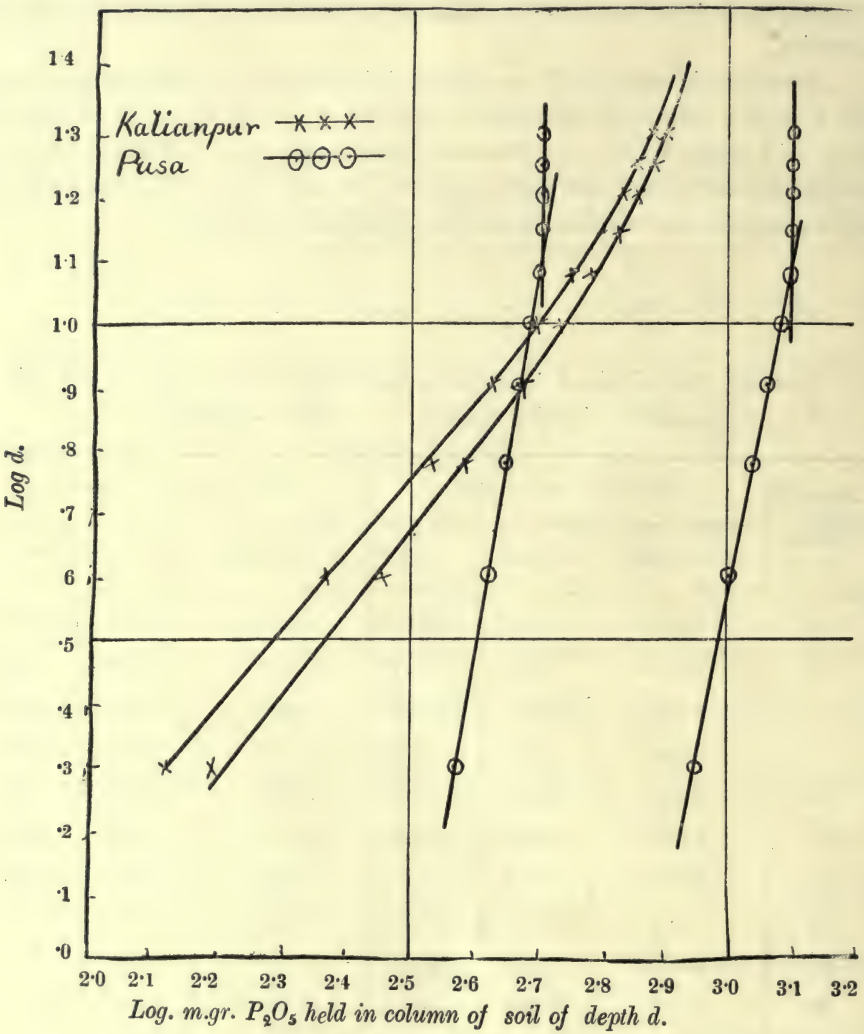
Showing the calculated and the experimental values obtained for the quantity of P_2O_5 held in a column of soil.

Depth of soil column d	KALIANPUR SOIL (dry)			KALIANPUR SOIL (moist)		
	H calculated	H found	Error	H calculated	H found	Error
2	0·1357	0·1312	— 0·0045	0·1540	0·1541	+ 0·0001
4	0·2518	0·2334	— 0·0184	0·2820	0·2880	+ 0·0060
6	0·3512	0·3420	— 0·0092	0·3886	0·3860	— 0·0026
8	0·4362	0·4260	— 0·0102	0·4771	0·4754	— 0·0017
10	0·5089	0·5014	— 0·0075	0·5508	0·5420	— 0·0088
12	0·5712	0·5661	— 0·0051	0·6121	0·6064	— 0·0057
14	0·6244	0·6331	+ 0·0087	0·6631	0·6662	+ 0·0031
16	0·6700	0·6825	+ 0·0125	0·7055	0·7204	+ 0·0149
18	0·7090	0·7221	+ 0·0131	0·7407	0·7664	+ 0·0257
20	0·7423	0·7590	+ 0·0167	0·7700	0·7983	+ 0·0283

Turning now to the results from the Pusa soils it will be found that when the logarithm of the total P_2O_5 in milligrams held in a column of soil is plotted against the log of the depth of the column, a straight line results up to 12 inches depth. Above that depth the curve is broken and the phenomenon of retention may be taken as ceasing at that point.

DIAGRAM VII.

Showing curves produced on plotting log total P_2O_5 (m.gr.) held in column of soil against log depth of column.



Therefore log H = A + B log d,

where d = column of soil in inches.

H = m.gr. P_2O_5 held in column d,

and A and B are constants equal to 2·5271 and 0·16 respectively for the moist soil, and 2·893 and 0·194 for the dry soil.

The calculated and the experimental values are contrasted in the following table.

TABLE XVIII.

Showing the calculated and the experimental values obtained for the quantity of P_2O_5 held in a column of soil.

	Moist			Dry		
Depth of soil	P_2O_5 present	P_2O_5 calculated	Error	P_2O_5 present	P_2O_5 calculated	Error
0″– 2″	0·3764	0·3761	– 0·0003	0·8915	0·8916	+ 0·0001
0″– 4″	0·4211	0·4201	– 0·0010	1·0132	1·0170	+ 0·0038
0″– 6″	0·4452	0·4483	+ 0·0031	1·0931	1·0985	+ 0·0054
0″– 8″	0·4683	0·4695	+ 0·0012	1·1548	1·1600	+ 0·0052
0″–10″	0·4879	0·4865	– 0·0014	1·2131	1·2110	– 0·0021
0″–12″	0·5044	0·5010	– 0·0034	1·2661	1·2530	– 0·0131
0″–14″	0·5071	0·5134	+ 0·0063	1·2891	1·2910	+ 0·0019
0″–16″	0·5084	0·5246	+ 0·0162	1·3131	1·3240	+ 0·0109
0″–18″	0·5095	0·5344	+ 0·0249	1·3228	1·3540	+ 0·0312
0″–20″	0·5106	0·5436	+ 0·0330	1·3384	1·3810	+ 0·0426

From the general formula $\log H = A + k \log d$, or $H = ad^k$ for the total P_2O_5 held in a column of soil, the amount of P_2O_5 held in any section can be deduced.

Let T = the amount of P_2O_5 in m.gr. held in a section at depth d.

Then T = P_2O_5 in column d—P_2O_5 in column (d—2)

$$= ad^k - a(d-2)^k$$

$$= a\{d^k - (d-2)^k\}$$

For the moist soil a = 336·6 and k = 0·16, and for the dry soil a = 781·6 and k = 0·194. The following table shows the calculated and the experimental values for the sections.

TABLE XIX.

Showing the calculated and the experimental values obtained for the quantity of P_2O_5 held in section.

	Dry soil			Moist soil		
Section	Found	Calculated	Error	Found	Calculated	Error
0″– 2″	0·8915	0·8916	– 0·0001	0·3764	0·3761	+ 0·0003
2″– 4″	0·1217	0·1259	– 0·0042	0·0447	0·0438	+ 0·0009
4″– 6″	0·0799	0·0813	– 0·0014	0·0241	0·0283	– 0·0042
6″– 8″	0·0617	0·0618	– 0·0001	0·0231	0·0212	+ 0·0019
8″–10″	0·0583	0·0500	+ 0·0083	0·0196	0·0172	+ 0·0024
10″–12″	0·0530	0·0422	+ 0·0108	0·0165	0·0141	+ 0·0024
12″–14″	0·0230	0·0375	– 0·0145	0·0027	0·0125	– 0·0098
14″–16″	0·0240	0·0336	0·0096	0·0013	0·0111	– 0·0098
16″–18″	0·0097	0·0297	– 0·0200	0·0011	0·0101	– 0·0090
18″–20″	0·0156	0·0274	– 0·0118	0·0011	0·0091	– 0·0080

It is evident from the preceding that the distribution of the P_2O_5 through columns of the type soils is regulated by strictly defined laws which, however, are very different in each case.

In the case of the Kalianpur soil the regulating expression is $\log T = a - kd$, which works out to $T = \frac{151{\cdot}0}{(1{\cdot}073)^d}$ in the case of dry soil, and $T = \frac{190{\cdot}5}{(1{\cdot}092)^d}$ for moist soils. Consequently as d increases, the amount held in each succeeding section gradually decreases.

With Pusa soil the corresponding regulating expression is $T = a\{d^k - (d-2)^k\}$.

From this it follows that in the first section $T = a \cdot 2^k$, whereas in the second section $T = a(4^k - \cdot 2^k)$. As k varies from about $\frac{1}{6}$ to $\frac{1}{5}$, T in the first section is approximately equal to a, but in the second and succeeding sections it is only a small fraction of a. Consequently the major portion of the P_2O_5 is held in the surface section. Further, as d increases, the difference between d^k and $(d-2)^k$ rapidly approaches zero which, in effect, means that the P_2O_5 cannot penetrate in appreciable quantities below a very limited depth.

Thus, in non-calcareous soils the superphosphate tends to distribute itself through the soil in a comparatively uniform manner, whereas in calcareous soils its distribution is restricted and the major portion of it is concentrated in the surface layers.

That this difference in the behaviour of the type soils to superphosphate is determined by the $CaCO_3$ content of the soil is readily demonstrated by instituting percolation experiments with the Kalianpur soil with which a proportion of finely divided $CaCO_3$ has been intimately mixed.

Distribution of P_2O_5 through a mixture of the Kalianpur soil with 5 per cent. $CaCO_3$. A percolation experiment was carried out in a similar manner to the preceding with the Kalianpur soil to which 5 per cent. of $CaCO_3$ had been intimately mixed. The experimental values obtained were as follows :—

TABLE XX.

Showing distribution of P_2O_5 through a mixture of Kalianpur soil with 5 per cent. $CaCO_3$.

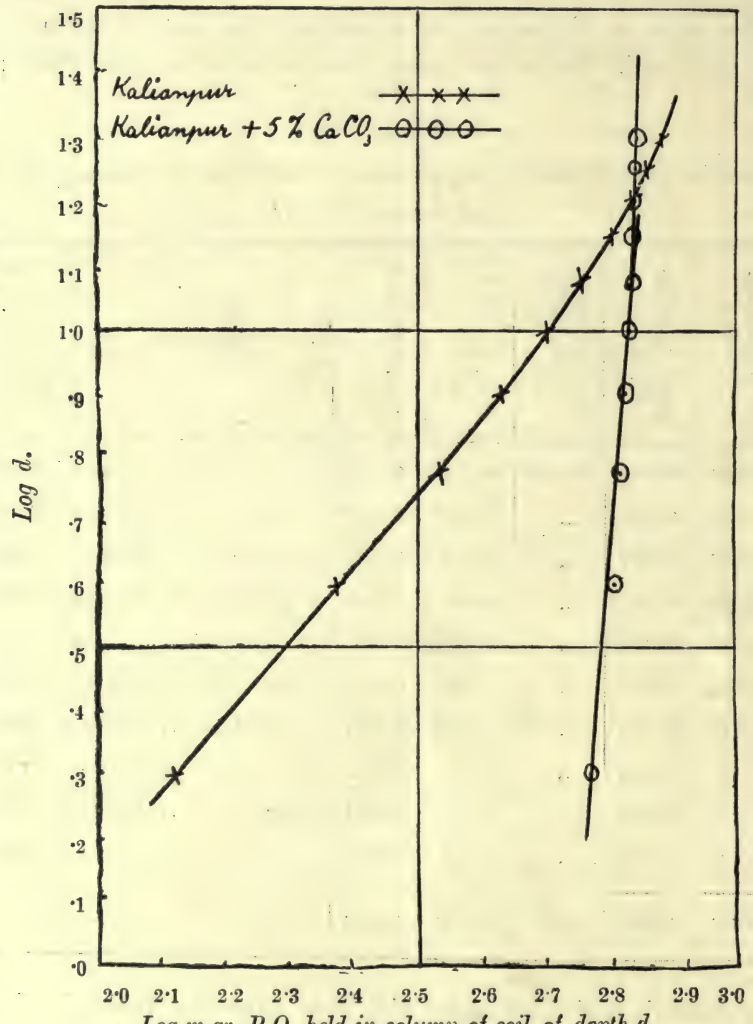
Section	P_2O_5 present in solution	Total insoluble P_2O_5	P_2O_5 originally present in the soil	P_2O_5 retained by soil	Total P_2O_5 held in section	Remarks		Corrected values: Total P_2O_5 held in each section T	Corrected values: Per cent. of original P_2O_5 held by soil in each section
0″– 2″	0·0224	0·6068	0·0589	0·5479	0·5703		grm.	0·5987	86·4
2″– 4″	0·0043	0·0953	,,	0·0364	0·0407		P_2O_5	0·0427	6·2
4″– 6″	0·0027	0·0697	,,	0·0108	0·0135	Percolate ..	0·0003	0·0142	2·0
6″– 8″	0·0026	0·0657	,,	0·0068	0·0094	Retained by soil	0·6199	0·0099	1·4
8″–10″	0·0028	0·0653	,,	0·0064	0·0092	Present in solu-		0·0097	1·4
10″–12″	0·0024	0·0617	,,	0·0028	0·0052	tion ..	0·0401	0·0055	0·8
12″–14″	0·0018	0·0613	,,	0·0024	0·0042	Total ..	0·6603	0·0044	0·6
14″–16″	0·0011	0·0609	,,	0·0020	0·0031	P_2O_5 taken ..	0·6933	0·0033	0·5
16″–18″	traces	0·0613	,,	0·0024	0·0024	Error ..	0·0330	0·0025	0·4
18″–20″	traces	0·0609	,,	0·0020	0·0020			0·0021	0·3
Total	0·0401	1·2089	0·5890	0·6199	0·6600			0·6930	

A comparison of these results with those given in Tables XIV and XV shows that by the addition of 5 per cent. $CaCO_3$ to the Kalianpur soil the

character of the retention has been changed and brought into line with that of the Pusa soil. This is clearly brought out in the following diagram where the log (P_2O_5 held in column of soil of depth d), *i.e.*, log H is plotted against log d for the Kalianpur soil, and the Kalianpur soil plus 5 per cent. $CaCO_3$.

DIAGRAM VIII.

Showing curves produced on plotting log total P_2O_5 (m.gr.) held in column of soil against log depth of column.



The fact that the addition of $CaCO_3$ to Kalianpur soil causes the retention and distribution of P_2O_5 through the soil to assume the characteristics of the Pusa soil, demonstrates clearly that it is the cause of the retention in calcareous soils and that the retention of superphosphate in these soils is due to the formation of more insoluble calcium phosphates as distinct from the physical retention in non-calcareous soils.

The position attained from a comparison of the results of these percolation experiments may be summarized as follows :—

1. The distribution of superphosphate through a non-calcareous soil by percolation is of a uniform type and is a function of the depth of percolation. The P_2O_5 penetrates to a considerable depth in accordance with the laws of adsorption, and consequently the effect of applications of superphosphate to such soils is widespread.

2. The distribution in the case of calcareous soils is of a non-uniform type the major portion of the P_2O_5 being held in the top layers of soil. Consequently the application of superphosphate to these soils has a very restricted effect and has therefore probably much less efficiency than equivalent amounts applied to soils of the opposite type.

3. In proportion to the amount of superphosphate applied to the columns of soil, the soil solution of calcareous soils contains a much less concentration of P_2O_5 than in the case of non-calcareous soils. In the light of present knowledge this can only mean that the P_2O_5 retained is in a much more available form in the latter soils.

4. That carbonate of lime is the main factor in determining the range of action and distribution of P_2O_5 in the soil is shown by the fact that when $CaCO_3$ is added to a non-calcareous soil, the experimental results then conform to the type found in calcareous soils. The retention of superphosphate in the latter is of a chemical nature due to the formation of insoluble calcium phosphates, and distinct from the physical retention of non-calcareous soils.

This being the case, it would seem very probable that if soluble phosphates, which have little or no chemical reaction with $CaCO_3$, were applied to calcareous soils, then the distribution of P_2O_5 would be mainly due to adsorption, and would be of a much more uniform type, resulting in increased efficiency. To test this point, a percolation experiment was carried out with a solution of di-sodium phosphate and Pusa soil. The results obtained were as follows :—

TABLE XXI.

Showing the results obtained from the percolation of di-sodium phosphate solution through Pusa soil.

Section	P_2O_5 present in solution	Total insoluble P_2O_5	P_2O_5 originally present in the soil	P_2O_5 retained by soil	Soluble and insoluble P_2O_5 held in section	Remarks		Corrected values: Total P_2O_5 held in each section	Corrected values: Per cent. of original P_2O_5 held in each section
							grm. P_2O_5		
0″– 2″	0·0243	0·1861	0·0192	0·1669	0·1912	Percolate ..	0·0019	0·2084	29·1
2″– 4″	0·0247	0·0498	,,	0·0306	0·0553			0·0602	8·4
4″– 6″	0·0273	0·0507	,,	0·0315	0·0588	P_2O_5 in solution	0·2786	0·0641	8·9
6″– 8″	0·0293	0·0494	,,	0·0302	0·0595			0·0649	9·0
8″–10″	0·0315	0·0503	,,	0·0311	0·0626	P_2O_5 insoluble .	0·3800	0·0682	9·5
10″–12″	0·0324	0·0476	,,	0·0284	0·0608			0·0663	9·1
12″–14″	0·0293	0·0406	,,	0·0214	0·0507	Total ..	0·6605	0·0553	7·7
14″–16″	0·0302	0·0326	,,	0·0134	0·0436	P_2O_5 taken ..	0·7197	0·0475	6·6
16″–18″	0·0278	0·0362	,,	0·0170	0·0448			0·0488	6·8
18″–20″	0·0218	0·0287	,,	0·0095	0·0313	Error ..	0·0592	0·0341	4·7
Total	0·2786	0·5720	0·1920	0·3800	0·6586			0·7178	

The results are not strictly parallel to any obtained before, but they conform more nearly to the type of distribution found with the Kalianpur soil than with the Pusa soil, when superphosphate was used :—

1. A comparatively small amount of P_2O_5 is retained by the first section of soil and the retained P_2O_5 is distributed more uniformly through the column of soil than was the case with superphosphate.

2. The amount of P_2O_5 in solution in each section is high and is fairly uniformly distributed.

3. The soluble P_2O_5 percolates to the deep layers and is there found in a comparatively high concentration.

It is, therefore, evident, that by using dressings of soluble phosphates, which have little or no reaction with $CaCO_3$, in place of superphosphate on calcareous soils, a much more uniform distribution of the P_2O_5 throughout the soil can be attained.

Provided that these phosphates are suitable for plant food, this wider distribution can only result in a wider and deeper root action and better cropping in such soils.

SUMMARY AND GENERAL CONCLUSIONS.

1. Retention of the P_2O_5 of superphosphate only occurs through adsorption in soils which are practically devoid of $CaCO_3$ or other substances capable of reacting with the acid salt. In presence of the latter the retention is due almost entirely to chemical combination resulting in the formation of comparatively insoluble compounds.

2. Generally, the first combination formed is that of di-calcic phosphate, $CaHPO_4$, and this reaction takes place very rapidly. Afterwards the di-calcic phosphate slowly reacts with more $CaCO_3$ forming tri-calcic phosphate, $Ca_3(PO_4)_2$.

3. As the reaction between superphosphate and $CaCO_3$ is very rapid, the range of action of the former is very limited. Further, the reaction between $CaCO_3$ and *dissolved* $CaHPO_4$ is again very rapid so that even this secondary reaction is very localized.

4. The very localized action of superphosphate in calcareous soils is demonstrated by percolation experiments in which it is shown that most of the P_2O_5 is retained in the surface layers. On the other hand, in non-calcareous soils penetration of the P_2O_5 takes place in appreciable quantity into the deep layers. The addition of a small quantity of $CaCO_3$ to a non-calcareous soil brings about a distribution of P_2O_5 analogous to that in calcareous soils showing that $CaCO_3$ is the determining agent.

5. It has been shown that even in calcareous soils the retention of the P_2O_5 of soluble phosphates having a neutral or alkaline reaction (*e.g.*, the phosphates of soda) is due to adsorption, and percolation experiments with such soils and phosphates show that a very even distribution of P_2O_5 can be attained. It would, therefore, seem very probable that such phosphates would be more efficacious than superphosphate in calcareous soils. This point is under investigation.

6. The phosphate manuring of calcareous soils is obviously a very different problem to that of non-calcareous soils and requires special study.

7. Although $CaHPO_4$ is formed in the first instance when superphosphate is applied to calcareous soils, the amount of P_2O_5 held in the soil solution does

not depend upon the solubility of this substance, but rather upon the proportion of Ca-ions in the solution, the presence of which reduces the amount of P_2O_5 in solution very considerably. Consequently manuring with superphosphate is relatively much more inefficient in calcareous than in non-calcareous soils.

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